



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 587 156 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
19.10.2005 Bulletin 2005/42

(51) Int Cl.7: **H01M 4/58**

(21) Application number: **03782865.4**

(86) International application number:
PCT/JP2003/016416

(22) Date of filing: **22.12.2003**

(87) International publication number:
WO 2004/064180 (29.07.2004 Gazette 2004/31)

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**

(72) Inventors:
• **KAJIYA, Yoshio, c/o Petoca Materials Ltd.
Kashima-gun, Ibaraki 314-0198 (JP)**
• **TASAKI, Hiroshi, c/o Petoca Materials Ltd
Kashima-gun, Ibaraki 314-0198 (JP)**

(30) Priority: **08.01.2003 JP 2003001955**

(71) Applicant: **Nikko Materials Co., Ltd.
Tokyo 105-8407 (JP)**

(74) Representative: **Goddard, Heinz J.
Forrester & Boehmert
Pettenkoferstrasse 20-22
80336 München (DE)**

(54) **MATERIAL FOR POSITIVE ELECTRODE OF LITHIUM SECONDARY BATTERY AND PROCESS
FOR PRODUCING THE SAME**

(57) Stable supply of a cathode material for a lithium secondary battery that excels in sinterability and composition stability and can exhibit satisfactory battery performance is accomplished by reducing to 100 ppm or less both the contents of Na and S being impurity ele-

ments in multiple oxides as materials for a cathode material for a lithium secondary battery and carbonic salts as precursor materials for the production of a cathode material for a lithium secondary battery.

Description

TECHNICAL FIELD

[0001] The invention relates to a cathode material for a lithium secondary battery (a precursor material for production of a cathode active material, and the cathode active material), contributing to enhancement in battery performance, and a method of producing the same

BACKGROUND TECHNOLOGY

[0002] There has lately been seen rapid increase in demand for nonaqueous lithium ion battery (lithium secondary battery) regarded as a high energy-density battery, and researches for enhancement in performance thereof from various angles have been under way

[0003] The lithium secondary battery is comprised of three basic elements, namely, "a cathode", "an anode", and "a separator retaining an electrolyte", interposed between the cathode, and the anode. For the cathode and the anode, use is made of "a slurry prepared by mixing, and dispersing an active material, an electroconductive material, a binding agent, and a plasticizer, where necessary, into a dispersion medium", applied to a current collector, such as a metal foil, metal mesh, and so forth.

[0004] For a cathode active material among those materials, there have been used a multiple oxide of lithium and a transition metal, such as a cobalt base multiple oxide ($\text{Li}_{1-x}\text{CoO}_2$), a nickel base multiple oxide ($\text{Li}_{1-x}\text{NiO}_2$), and a manganese base multiple oxide ($\text{Li}_{1-x}\text{Mn}_2\text{O}_4$), and there have so far been proposed material shown as follows, and so forth.

a) a multiple oxide expressed by chemical formula $\text{A}_x\text{M}_y\text{N}_z\text{O}_2$ (A is at least an element selected from the group of alkaline metals, M is a transition metal, N is at least an element selected from the group consisting of Al, In, and Sn, and x, y, and z are numeric values defined by $0.05 \leq x \leq 1.10$, $0.85 \leq y \leq 1.00$, and $0.001 \leq z \leq 0.10$, respectively) (refer to JP 62-90863 A)

b) a multiple oxide expressed by chemical formula $\text{Li}_x(\text{Co}_{1-y}\text{Ni}_y)\text{O}_2$ (where x is a numeric value in a range of 0 to 2, and y is a numeric value in a range of 0.5 to 0.9) (refer to JP 1-294364 A)

c) a multiple oxide expressed by chemical formula $\text{Li}_x\text{Co}_{1-y}\text{M}_y\text{O}_2$ (where $0.85 \leq x \leq 1.3$, $0.05 \leq y \leq 0.35$, and M is at least an element selected from the group consisting of W, Mn, Ta, Ti, and Nb (refer to JP 3-201368 A)

d) a multiple oxide expressed by chemical formula $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ (where $0.02 \leq x \leq 0.35$) (refer to JP 4-28162 A)

e) a multiple oxide expressed by chemical formula $\text{Li}_y\text{Ni}_{1-x}\text{Mn}_x\text{O}_2$ (where $0 \leq x \leq 0.3$, $0 \leq y \leq 1.3$) (refer to JP6-96768 A)

f) a multiple oxide expressed by chemical formula $\text{LiNi}_x\text{Mn}_{1-x}\text{O}_2$ (where $0.95 \geq x \geq 0.70$) (refer to JP 8-171910 A)

g) a multiple oxide expressed by chemical formula $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ (where $0.95 \geq x \geq 0.50$) (refer to JP 8-222220 A)

h) a multiple oxide expressed by chemical formula $\text{Li}_x(\text{Co}_{1-y}\text{Ni}_y)\text{O}_2$ (where $0 < x < 1$, $0.75 < y \leq 0.9$) (refer to JP 8-236117 A)

i) a multiple oxide expressed by chemical formula $\text{Li}_x(\text{Ni}_{1-y}\text{Co}_y)\text{O}_2$ (where $0.95 \leq x \leq 1.2$, $0 \leq y \leq 0.5$) (refer to JP 9-251854 A)

j) a multiple oxide expressed by chemical formula $\text{LiCo}_{1-p}\text{Ni}_p\text{O}_2$ (where $0.95 \leq p \leq 0.9$) (refer to JP 9-259884 A)

k) a multiple oxide expressed by chemical formula $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ (where $0 \leq x \leq 1.2$, $0 \leq y \leq 0.5$) (refer to JP 9-270257 A)

l) a multiple oxide expressed by chemical formula $\text{Li}_{1-a}\text{Ni}_{1-b-c-d}\text{Mn}_b\text{Co}_c\text{M}_d\text{O}_2$ (provided that M is at least one trace additive element, other than H and Li, selected from elements of the Groups Ia, IIa, IIb, IIIb, and IVb, respectively, and transition elements, other than Ni, Co, and Mn, where $0.15 \leq a \leq 0.10$, $0.02 \leq b \leq 0.45$, $0 \leq c \leq 0.50$ and $0 \leq d \leq 0.20$) (refer to JP 11-307094 A)

[0005] The above described lithium multiple oxides for use as the cathode material for the lithium secondary battery is generally synthesized by mixing a compound of an element serving as the main component of the cathode material for the lithium secondary battery (carbonate, oxide, and so forth, of Co, Ni, Mn, and so forth) with a lithium compound ((lithium carbonate, etc.) at a predetermined mixing ratio before heat treatment is applied thereto.

[0006] For example, in JP 1-294364 A, described as above, there is disclosed "a method of producing a layered lithium multiple oxide, comprising the steps of saturating an aqueous solution containing chlorides of Ni and Co, respectively, with carbon dioxide gas (carbonic acid gas), adding an aqueous solution of sodium bicarbonate to the aqueous solution to be subsequently left out as it is, thereby causing the respective carbonates of Ni, and Co to undergo coprecipitation, washing precipitates as obtained before drying in argon gas at 140°C , and subsequently mixing the precipitates with lithium carbonate before heating a mixture in the air to thereby cause reaction".

[0007] Further, in JP 11-307094 A, described as above, there is disclosed "a method of producing lithium multiple oxides, comprising the steps of adding an aqueous solution of sulfates of respective constituent elements other than lithium, and an aqueous solution of ammonium hydrogencarbonate, with a trace of ammonium added thereto, into a reactor cell little by little, and concurrently or alternately, causing uniform crystal growth of a multiple salt to take place in a substantially concentric manner while keeping a pH value of a mixed solution, in a neutral region, and subsequently mixing a multiple salt as obtained with lithium hydroxide to be thereby heated in an oxygen gas flowing atmosphere so as to be sintered."

[0008] The inventor, et al., however, have found out through examination on performance of lithium secondary batteries in which various lithium multiple oxides are adopted as the cathode material for the lithium secondary battery that the lithium multiple oxides used in the past are not fully satisfactory in respect of sinterability, composition stability, and so forth, leading to deterioration in battery performance (rate performance, and so forth).

[0009] Under the circumstances, it is an object of the invention to establish means for stable supply of a cathode material for a lithium secondary battery, excellent in sinterability, and composition stability, and capable of exhibiting satisfactory battery performance.

DISCLOSURE OF THE INVENTION

[0010] To that end, the inventor, et al. have continued further studies, and as a result, have succeeded in obtaining the following knowledge.

(a) The more fine, and the more homogeneous a layered lithium multiple oxide for use as an active material for a cathode material for a lithium secondary battery is, the more excellent is battery performance as exhibited, however, in order to obtain a fine, and homogeneous lithium multiple oxide, raw material for production of the lithium multiple oxide need be fine, and homogeneous.

(b) As means for obtaining fine, and homogeneous lithium multiple oxide, there has been known a method of preparing fine carbonate by a wet process, and using the same as raw material, as disclosed in, for example, JP 1-294364 A, and JP 11-307094 A. However, if Na and S are contained as impurity elements in the raw material, the impurity elements have adverse effects on sinterability and composition stability, thereby creating a cause for deterioration in battery performance.

For example, with the method disclosed in JP 1-294364 A, sodium bicarbonate is used to cause coprecipitation of the carbonates, and consequently, contamination of the carbonate by Na is unavoidable, so that upon firing for production of a layered lithium multiple oxide, a specific surface area thereof increases resulting in not only deterioration in sinterability and interference with stability in operation, but also degradation in rate performance if a product is used as a cathode material for a lithium secondary battery.

With the method disclosed in JP 11-307094 A, described as above, since ammonium is used to cause the crystal growth of the multiple salt, nitrogen enters waste liquid, and consequently, not only costly treatment of the waste liquid is required, but also contamination of the multiple salt by sulfur (S) occurs because the aqueous solution of the sulfates is used, so that sulfur reacts with lithium to form lithium sulfide, thereby not only interfering with composition stability of the cathode material, but also inviting deterioration in battery performance.

(c) In contrast, if an aqueous solution of Ni chloride, Mn chloride, and Co chloride (or a mixed liquid of the aqueous solution described, and an aqueous solution of chloride of at least one element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr,) is charged into lithium carbonate suspension, thereby precipitating carbonate, if the aqueous solution of Ni chloride, Mn chloride, and Co chloride (or the mixed liquid of the aqueous solution described, and the aqueous solution of chloride of at least one element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr,) is dripped into an aqueous solution of lithium hydrogencarbonate prepared by blowing carbon dioxide gas (CO₂ gas) into an aqueous solution of lithium carbonate, and concurrently a pH value of the aqueous solution is raised, thereby precipitating carbonate, or if the aqueous solution of lithium hydrogencarbonate prepared by blowing carbon dioxide gas (CO₂ gas) into the aqueous solution of lithium carbonate is dripped or charged into the aqueous solution of Ni chloride, Mn chloride, and Co chloride (or the mixed liquid of the aqueous solution as described, and the aqueous solution of chloride of at least one element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), and concurrently, the pH value of the aqueous solution is raised, thereby precipitating carbonate, it is possible to obtain carbonate of Ni, Mn, and Co, in ultrafine particle form, (or a mixture of the carbonate thereof, and carbonate as well as hydroxide of at least one element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), without contamination by Na and S (not more than 100 ppm in mass percentage, respectively). Thereafter, the carbonate, and the mixture, obtained as above, are subjected to oxidation treatment to be turned into an oxide, and subsequently, the oxide is mixed with a lithium source (lithium carbonate, and so forth) to be thereby fired, whereupon there is obtained a layered lithium multiple oxide without contamination by Na and S (not more than 100 ppm in mass percentage, respectively). and high in tap density, and when the

lithium multiple oxide is used as a cathode active material for a lithium secondary battery, the lithium secondary battery stably exhibiting excellent battery performance can be implemented. Furthermore, even in the case where the carbonate (or the mixture) obtained by dripping the aqueous solution of Ni chloride, Mn chloride, and Co chloride (or the mixed liquid of the aqueous solution as described, and the aqueous solution of the chloride of at least one element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr) into the aqueous solution of lithium hydrogencarbonate, and concurrently, by raising the pH value of the aqueous solution, as it is without the oxidation treatment applied thereto, and the carbonate (or the mixture) obtained by dripping, and charging the aqueous solution of lithium hydrogencarbonate into the aqueous solution of Ni chloride, Mn chloride, and Co chloride (or the mixed liquid of the aqueous solution as described, and the aqueous solution of the chloride of at least one element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), and concurrently, by raising the pH value of the aqueous solution, as it is without the oxidation treatment applied thereto, are mixed with the lithium source to be thereby fired, it is possible to produce an excellent lithium multiple oxide with correspondingly little contamination by Na and S.

[0011] The invention has been developed based on above-described items of the knowledge, and so forth, providing a cathode material for a lithium secondary battery (a precursor material (carbonate and a mixture of the carbonate and hydroxide) for production of a cathode active material, and lithium multiple oxides serving as the cathode active material), and a method of producing the same, as shown under the following items 2 through 9:

(2) a precursor material for a cathode material for a lithium secondary battery, being a mixture of carbonate expressed by chemical formula ACO_3 (where A is at least an element selected from the group consisting of Ni, Mn and Co), and either or both of carbonate expressed by chemical formula DCO_3 (where D is at least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), and hydroxide expressed by chemical formula $\text{D}(\text{OH})$, an atomic ratio of an element D to the total of the element A and the element D $\{D / (A + D)\}$ being in a range of 0 to 0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage.

(3) a cathode material for a lithium secondary battery produced by use of the precursor material as set forth in the above item (2), being an Li-A-DO based multiple oxide for the lithium secondary battery (where A is at least an element selected from the group consisting of Ni, Mn and Co, and D is at least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), an atomic ratio of the element D to the total of the element A and the element D $\{D / (A + D)\}$ being in a range of exceeding 0 to not more than 0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage.

(4) a method of producing a precursor material for a cathode material for a lithium secondary battery, expressed by chemical formula ACO_3 (where A is at least an element selected from the group consisting of Ni, Mn and Co) with respective contents of Na, and S, as impurity elements, at not more than 100 ppm in mass percentage, said method comprising the steps of charging an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride into lithium carbonate suspension, and precipitating carbonate.

(5) a method of producing a precursor material for a cathode material for a lithium secondary battery, being a mixture of carbonate expressed by chemical formula ACO_3 (where A is at least an element selected from the group consisting of Ni, Mn and Co), and either or both of carbonate expressed by chemical formula DCO_3 (where D is at least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), and hydroxide expressed by chemical formula $\text{D}(\text{OH})$, an atomic ratio of an element D to the total of the element A and the element D $\{D / (A + D)\}$ being in a range of 0 to 0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage, said method comprising the steps of charging a mixed liquid composed of an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and an aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride into lithium carbonate suspension, and precipitating carbonate, or carbonate, and hydroxide.

(6) a method of producing a precursor material for a cathode material for a lithium secondary battery, composed of a carbonate expressed by chemical formula ACO_3 (where A is at least an element selected from the group consisting of Ni, Mn and Co) with respective contents of Na, and S, as impurity elements, at not more than 100 ppm in mass percentage, said method comprising the steps of preparing an aqueous solution of lithium hydrogen-carbonate by blowing carbon dioxide gas into an aqueous solution of lithium carbonate, dripping an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride to the aqueous solution of lithium hydrogencarbonate, or dripping or charging the aqueous solution of lithium hydrogencarbonate into the aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and subsequently driving out dissolved carbon dioxide gas

by aerating the aqueous solution, thereby raising a pH value of the aqueous solution to cause carbonate to be precipitated.

(7) a method of producing a precursor material for a cathode material for a lithium secondary battery, being a mixture of carbonate expressed by chemical formula ACO_3 (where A is at least an element selected from the group consisting of Ni, Mn and Co), and either or both of carbonate expressed by chemical formula DCO_3 (where D is at least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), and hydroxide expressed by chemical formula D(OH) , an atomic ratio of an element D to the total of the element A and the element D $\{\text{D} / (\text{A} + \text{D})\}$ being in a range of 0 to 0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage, said method comprising the steps of preparing an aqueous solution of lithium hydrogencarbonate by blowing carbon dioxide gas into an aqueous solution of lithium carbonate, dripping a mixed liquid of an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and an aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride to the aqueous solution of lithium hydrogencarbonate, or dripping or charging the aqueous solution of lithium hydrogencarbonate into the mixed liquid of the aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and the aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride, and subsequently, driving out dissolved carbon dioxide gas by aerating the aqueous solution, thereby raising a pH value of the aqueous solution to cause carbonate to be precipitated.

(8) a method of producing a cathode material for a lithium secondary battery, being an Li-A-D-O based multiple oxide for the lithium secondary battery (where A is at least an element selected from the group consisting of Ni, Mn and Co, and D is at least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), an atomic ratio of the element D to the total of the element A and the element D $\{\text{D} / (\text{A} + \text{D})\}$ being in a range of 0 to 0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage, said method comprising the steps of charging a mixed liquid of an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and an aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride into lithium carbonate suspension, thereby precipitating carbonate, or carbonate, and hydroxide, and subsequently, mixing precipitate as obtained with a lithium source before firing, or applying oxidation treatment to the precipitate as obtained to be turned into an oxide, the oxide being mixed with the lithium source before firing.

(9) a method of producing a cathode material for a lithium secondary battery, being an Li-A-D-O based a multiple oxide for the lithium secondary battery (where A is at least an element selected from the group consisting of Ni, Mn and Co, and D is at least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), an atomic ratio of the element D to the total of the element A and the element D $\{\text{D} / (\text{A} + \text{D})\}$ being in a range of 0 to 0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage, said method comprising the steps of preparing an aqueous solution of lithium hydrogencarbonate by blowing carbon dioxide gas into an aqueous solution of lithium carbonate, dripping a mixed liquid of an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and an aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride to the aqueous solution of lithium hydrogencarbonate, or dripping or charging the aqueous solution of lithium hydrogencarbonate into the mixed liquid of the aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and the aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride, subsequently, driving out dissolved carbon dioxide gas by aerating the aqueous solution, thereby raising a pH value of the aqueous solution to cause carbonate, or carbonate and hydroxide to be precipitated, and mixing precipitate as obtained with a lithium source before firing, or applying oxidation treatment to the precipitate as obtained to be turned into an oxide, the oxide being mixed with the lithium source before firing.

BEST FORM FOR CARRYING OUT THE INVENTION

[0012] In a cathode material for a lithium secondary battery (a precursor material for production of a cathode active material, and the cathode active material), according to the invention, respective contents of Na, and S, as impurity elements, are set to 100 ppm or less because if Na content in any material (carbonates, and so forth, and lithium multiple oxides) exceeds 100 ppm, deterioration in battery performance becomes pronounced due to degradation in sinterability when the material is used as the cathode active material for the lithium secondary battery, and meanwhile, if S content in any material (carbonates, and so forth, and lithium multiple oxides) exceeds 100 ppm, deterioration in

battery performance also becomes pronounced due to interference with stability in material composition through formation of lithium sulfide.

[0013] Further, in order to secure excellent battery performance by stabilizing crystals of the cathode active material for the lithium secondary battery, as produced, the cathode active material for the lithium secondary battery may contain at least one element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr, and accordingly, a precursor material of the cathode active material for the lithium secondary battery may contain at least one element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr. In this case, however, if a ratio of total content of Mg, Al, Ti, Cr, Fe, Cu, or Zr to the sum of total content of Ni, Mn, or Co, as the main element of the cathode active material, and the precursor material, and the total content of Mg, Al, Ti, Cr, Fe, Cu, or Zr exceeds of 0.1 in atomic ratio, there will be shown a tendency of battery performance rather undergoing deterioration, so that precautions should be taken such that the ratio of the total content of Mg, Al, Ti, Cr, Fe, Cu, or Zr to the sum of the total content of Ni, Mn, or Co, and the total content of Mg, Al, Ti, Cr, Fe, Cu, or Zr falls in a range of 0 to 0.1 in atomic ratio.

[0014] Now, in producing a carbonate for use in the cathode material for the lithium secondary battery according to the method of the invention, lithium carbonate suspension is first prepared, or an aqueous solution of lithium hydrogencarbonate is prepared by blowing carbon dioxide gas (CO₂ gas) into an aqueous solution of lithium carbonate.

[0015] Appropriate concentration of lithium carbonate in a liquid to be prepared is in a range of about 20 to 600 g/ℓ. In the case of preparing the aqueous solution of lithium hydrogencarbonate, lithium carbonate concentration is preferably on the order of 30 g/ℓ, and in the case of preparing the suspension, the same is preferably on the order of 400 g/ℓ.

[0016] Since lithium hydrogencarbonate is an unstable substance, a process of preparing the aqueous solution of lithium hydrogencarbonate by blowing carbon dioxide gas into the aqueous solution of lithium carbonate is preferably executed immediately before the production of the carbonate for use in the cathode material for the lithium secondary battery.

[0017] Subsequently, an aqueous solution with a desired composition of Ni chloride, Mn chloride, and Co chloride is charged or dripped into the lithium carbonate suspension, as adjusted or the aqueous solution of lithium hydrogencarbonate, as adjusted, or the aqueous solution of lithium hydrogencarbonate is dripped or charged into the aqueous solution with the desired composition of Ni chloride, Mn chloride, and Co chloride. In this case, a small amount of an aqueous solution of a chloride of a different kind of metal, such as Mg, Al, Ti, Cr, Fe, Cu, Zr, Si, Ca, or so on, may be added thereto.

[0018] The aqueous solution of the chlorides, for use, may be adjusted in composition by modifying a blending ratio among the Ni chloride, Mn chloride, and Co chloride according to "composition of a carbonate to be produced", and depending on a carbonate to be obtained, the aqueous solution may be an aqueous solution of one of the Ni chloride, Mn chloride, and Co chloride, alone.

[0019] In this case, appropriate chloride concentration in the aqueous solution of the chlorides, is from 1.0 to 5.0 mol/ℓ in terms of total concentration of chlorides of Ni, Mn, Co, respectively, and an additive element, preferably from 1.5 to 3.0 mol/ℓ.

[0020] A dripping rate, or charging rate of the solution is preferably adjusted such that a total addition amount is added in from 10 minutes to 2 hours. For example, when the aqueous solution of the chlorides at a ratio of 30 liter in total addition amount is dripped into 140 liter of the aqueous solution of lithium hydrogencarbonate, the dripping rate is set to around 30 ℓ/hr. Further, when 50 liter of the aqueous solution of the chlorides is charged into 75 liter of the lithium carbonate suspension (lithium carbonate: 180 g/ℓ), 50 liter thereof is charged in around 30 minutes. In the case of dripping or charging 140 liter of the aqueous solution of lithium hydrogencarbonate into 30 liter of the aqueous solution of the chlorides, the dripping or charging rate is set to on the order of 100 ℓ/hr.

[0021] As for liquid temperature, either of the solutions is may be at room temperature, but may be heated up. Further, when dripping (charging) the aqueous solution of the chlorides, the lithium carbonate suspension (the aqueous solution of lithium hydrogencarbonate) is preferably stirred at a stirring rate of 50 to 400 rpm. The stirring rate is decided upon according to a reactor cell.

[0022] Depending on the dripping (charging) rate, and stirring rate, carbonate of desired grain size can be obtained. It is preferable from the viewpoint of better stability in operation to adopt a batch method in carrying out dripping (charging) of the aqueous solution of the chlorides into the lithium carbonate suspension (the aqueous solution of lithium hydrogencarbonate) as prepared. However, a process may be adopted whereby while the aqueous solution of lithium hydrogencarbonate is continuously prepared by blowing carbon dioxide gas into the aqueous solution of lithium carbonate, the aqueous solution of the chlorides is continuously dripped (continuously added) into the aqueous solution of lithium hydrogencarbonate, as prepared.

[0023] Next, in the case of dripping the aqueous solution of the chlorides into the aqueous solution of lithium hydrogencarbonate, or in the case of dripping or charging lithium hydrogencarbonate into the aqueous solution of the chlorides, dissolved carbon dioxide gas is driven out (expelled) by aerating the solution after the other solution is dripped or added thereto, thereby raising a pH value of the aqueous solution (raising the pH value from about 6.7 to about 8.3) to cause carbonate to be precipitated.

[0024] In this case, because carbonates of Ni, Mn, and Co, respectively, occurring by reaction between the aqueous solution of lithium hydrogencarbonate and the aqueous solution of the chlorides, have solubility against the solution present around the carbonates, and are resolved in the solution, it is necessary for implementing satisfactory precipitation of the carbonates to raise a pH value by driving out the carbon dioxide gas dissolved. As a method of driving out the carbon dioxide dissolved, "a method of heating solution", "a method of adding alkali", and so forth may be adopted, however, an aerating method, which is the simplest and inexpensive method, is regarded preferable from an industrial point of view.

[0025] In the case of charging the aqueous solution of the chlorides into the lithium carbonate suspension, reaction occurs at a higher pH value, so that there is no need for driving out the carbon dioxide gas by aeration. Accordingly, carbonate as desired can be very simply obtained.

[0026] In other words, with the use of the lithium carbonate suspension, yield per batch can be further enhanced.

[0027] With the process described as above, it is possible to obtain carbonate in fine particle form, 5 to 10 μm in average grain size, with Na content, and S content, not more than 100 ppm, respectively.

[0028] The carbonate in fine particle form, obtained as above, is subjected to oxidation treatment (firing in an oxidizing atmosphere, and so forth) according the conventional method to be turned into an oxide, and the oxide is mixed with a lithium source (lithium carbonate, and so forth) to be thereby fired, whereupon there is obtained a layered lithium multiple oxide not more than 100 ppm in Na content, and S content, respectively, and high in tap density, and when the lithium multiple oxide is used as a cathode material (active material) for a lithium secondary battery, a lithium secondary battery excellent in battery performance (rate performance) can be implemented.

[0029] In production of the lithium multiple oxide described as above, the carbonate in fine particle form, as it is, without the oxidation treatment applied thereto, may be mixed with the lithium source to be thereby fired.

[0030] Further, Li-A-O (where A is at least an element selected from the group consisting of Ni, Mn and Co) based multiple oxides for a cathode of a lithium secondary battery is effective for enhancement in battery performance if the respective contents of Na, and S are set to 100 ppm or less.

[0031] Now, the invention is described hereinafter with reference to working examples.

(Working Example 1)

[0032] First, 0.4 liter of lithium carbonate suspension with lithium carbonate suspended in water (lithium carbonate concentration: 420 g/l) was prepared.

[0033] Next, while stirring the lithium carbonate suspension (at room temperature) at 300 rpm, 0.6 liter of an aqueous solution of a chloride of Ni, Mn, and Co, with composition of Ni : Mn : Co at 1 : 1 : 1 (the aqueous solution at room temperature, containing the chloride of Ni, Mn, and Co, at 2.9 mol/l in total concentration) was added to the lithium carbonate suspension at an addition rate of 0.3 l/hr.

[0034] As a result of processing described, precipitate in fine particle form was precipitated in the solution, and upon examination of material in fine particle form, obtained by filtering and separating the precipitate to be subsequently further washed and dried, it was confirmed that the material in fine particle form was a multiple carbonate 10.0 μm in average grain size, with composition of Ni : Mn : Co at 1 : 1 : 1.

[0035] Further, in the multiple carbonate, obtained as above, Na content was found at not more than 20 ppm and S content was found at not more than 10 ppm.

[0036] Subsequently, heat treatment at 650°C was applied to the multiple carbonate, obtained as above, for 15 hrs, whereupon there was obtained a multiple oxide in fine particle (10 μm in average grain size) with composition of Ni : Mn : Co at 1 : 1 : 1.

[0037] By mixing 100 g of the multiple oxide with 45.3 g of lithium carbonate, a mixture was obtained, and the mixture was fired in the air at 1050°C for 5 hrs.

[0038] Measurements on powders of a compound obtained as above were made by the powder X-ray diffraction method, whereupon it was confirmed that the powders represented a layered lithium multiple oxide expressed by chemical formula $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$.

[0039] Further, the lithium multiple oxide powders were found at 9.8 μm in average grain size, and 0.4 m^2/g in specific surface area, and Na content in the powders was 20 ppm while S content in the powders was on the order of not more than 10 ppm.

[0040] Then, examinations were conducted on the characteristics of a lithium secondary battery in which the lithium multiple oxide obtained as above was adopted as a cathode active material for the lithium secondary battery.

[0041] In conducting the examinations, slurry composed of 85 wt. % of the lithium multiple oxide obtained as the active material, 8 wt. % of acetylene black, and 7 wt. % of PVDF (polyvinylidene fluoride) was prepared by use of NMP (N-methyl-pyrrolidone) as a solvent, and the slurry was applied to an aluminum foil to be subsequently dried before press forming, thereby having obtained a cathode sample for use in evaluation of the lithium secondary battery.

[0042] The lithium secondary battery for use in the evaluation was a coin-battery model of 2032 type wherein the

cathode sample was used for the cathode thereof while a lithium foil was used for an opposite electrode thereof, and for an electrolyte thereof, use was made of a solvent where a ratio of EC (ethylene carbonate) / DMC (dimethyl carbonate) was at 1 : 1, in which LiPF_6 at 1 mol was dissolved.

[0043] Using the lithium secondary battery for the evaluation, discharge capacity, and current load performance (discharge capacity obtained at 0.5C / discharge capacity obtained at 0.2C) were examined, and examination results are shown in Table 1.

Table 1

	results of examinations	
	discharge capacity (mAh / g)	current load performance (discharge capacity obtained at 0.5C / discharge capacity obtained at 0.2C)
working example 1	152	> 98
working example 2	152	> 98
working example 3	152	> 98
working example 4	165	97
working example 5	166	96
comparative example 1	125	75
working example 6	152	> 98
working example 7	150	> 98

(Working Example 2)

[0044] Lithium carbonate was dissolved into water to prepare an aqueous solution of lithium carbonate, into which carbon dioxide gas was blown, having thereby prepared 140 liter of an aqueous solution of lithium hydrogencarbonate with lithium carbonate concentration at 30 g / ℓ .

[0045] Subsequently, while stirring the aqueous solution of lithium hydrogencarbonate (at room temperature) at 300 rpm, 30 liter of an aqueous solution of a chloride of Ni, Mn, and Co, with composition of Ni : Mn : Co at 1 : 1 : 1 (the aqueous solution at room temperature containing the chloride of Ni, Mn, and Co, at 1.5 mol / ℓ in total concentration) was dripped into the aqueous solution of lithium hydrogencarbonate at an addition rate of 30 ℓ / hr.

[0046] Next, through the intermediary of a vent pipe, air was passed at a flow rate of 10 ℓ / min through the solution to which addition of the aqueous solution of the chloride was completed, and the carbon dioxide gas dissolved in the solution was driven out, having thereby raised a pH value from 6.7 to 8.3.

[0047] As a result of processing described, precipitate in fine particle form was precipitated in the solution, and upon examination of material in fine particle form, obtained by filtering and separating the precipitate to be subsequently further washed and dried, it was confirmed that the material in fine particle form was a multiple carbonate 7 μm in average grain size, with composition of Ni : Mn : Co at 1 : 1 : 1.

[0048] Further, in the multiple carbonate, obtained as above, Na content was found in a range of 10 to 50 ppm, and S content was found at not more than 10 ppm.

[0049] Subsequently, heat treatment at 650°C was applied to the multiple carbonate, obtained as above, for 15 hrs, whereupon there was obtained a multiple oxide in fine particles (7 μm in average grain size) with composition of Ni : Mn : Co at 1 : 1 : 1.

[0050] By mixing 100 g of the multiple oxide with 45.3 g of lithium carbonate, a mixture was obtained, and the mixture was fired in the air at 1050°C for 5 hrs.

[0051] Measurements on powders of a compound obtained as above were made by the powder x-ray diffraction method, whereupon it was confirmed that the powders represented a layered lithium multiple oxide expressed by chemical formula $\text{Li Ni}_{0.33} \text{Mn}_{0.33} \text{Co}_{0.33} \text{O}_2$.

[0052] Further, the lithium multiple oxide powders were found at 7 μm in average grain size, and 0.4 m^2 / g in specific surface area, and Na content in the powders was in a range of 10 to 50 ppm while S content in the powders was on the order of not more than 10 ppm.

[0053] Then, examinations were conducted on the characteristics of a lithium secondary battery in which the lithium multiple oxide obtained as above was adopted as a cathode active material for the lithium secondary battery.

[0054] In conducting the examinations, slurry composed of 85 wt. % of the lithium multiple oxide obtained as the active material, 8 wt. % of acetylene black, and 7 wt. % of PVDF (polyvinylidene fluoride) was prepared by use of NMP

(N - methyl - pyrrolidone) as a solvent, and the slurry was applied to a aluminum foil, to be subsequently dried before press forming, thereby having obtained a cathode sample for use in evaluation of the lithium secondary battery.

[0055] The lithium secondary battery for use in the evaluation was the coin-battery model of 2032 type wherein the cathode sample was used for the cathode thereof while a lithium foil was used for an opposite electrode thereof, and for an electrolyte thereof, use was made of a solvent where a ratio of EC (ethylene carbonate) / DMC (dimethyl carbonate) was at 1 : 1, in which LiPF_6 at 1 mol was dissolved.

[0056] Using the lithium secondary battery for the evaluation, discharge capacity, and current load performance (discharge capacity obtained at 0.5C/discharge capacity obtained at 0.2C) were examined, and examination results, together with results for other lithium secondary batteries, are shown in Table 1.

(Working Example 3)

[0057] Lithium carbonate was dissolved into water to prepare an aqueous solution of lithium carbonate, into which carbon dioxide gas was blown, having thereby prepared 140 liter of an aqueous solution of lithium hydrogencarbonate with lithium carbonate concentration at 30 g / ℓ .

[0058] Subsequently, while stirring the aqueous solution of lithium hydrogencarbonate (at room temperature) at 300 rpm, 30 liter of an aqueous solution of a chloride of Ni, Mn, and Co, with composition of Ni : Mn : Co at 4 : 4 : 2 (the aqueous solution at room temperature, containing the chloride of Ni, Mn, and Co, at 1.5 mol/ ℓ in total concentration) was dripped into the aqueous solution of lithium hydrogencarbonate at an addition rate of 30 ℓ / hr.

[0059] Next, through the intermediary of a vent pipe, air was passed at a flow rate of 10 ℓ / min through the solution to which addition of the aqueous solution of the chloride was completed, and the carbon dioxide gas dissolved in the solution was driven out, having thereby raised a pH value from 6.7 to 8.3.

[0060] As a result of processing described, precipitate in fine particle form was precipitated in the solution, and upon examination of material in fine particle form, obtained by filtering and separating the precipitate to be subsequently further washed and dried, it was confirmed that the material in fine particle form was a multiple carbonate 7 μm in average grain size, with composition of Ni : Mn : Co at 4 : 4 : 2.

[0061] Further, in the multiple carbonate, obtained as above, Na content was found in a range of 10 to 50 ppm, and S content was found at 20 ppm.

[0062] Subsequently, heat treatment at 650°C was applied to the multiple carbonate, obtained as above, for 15 hrs, whereupon there was obtained a multiple oxide in fine particles (6 μm in average grain size) with composition of Ni : Mn : Co at 4 : 4 : 2.

[0063] By mixing 100 g of the multiple oxide with 45.1 g of lithium carbonate, a mixture was obtained, and the mixture was fired in the air at 1000°C for 10 hrs.

[0064] Measurements on powders of a compound obtained as above were made by the powder x-ray diffraction method, whereupon it was confirmed that the powders represented a layered lithium multiple oxide expressed by chemical formula $\text{Li Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$.

[0065] Further, the lithium multiple oxide powders were found at 6 μm in average grain size, and 0.7 m^2 / g in specific surface area, and Na content in the powders was in a range of 10 to 60 ppm while S content in the powders was 30 ppm.

[0066] Then, examinations were conducted on the characteristics of a lithium secondary battery in which the lithium multiple oxide obtained as above was adopted as a cathode active material for the lithium secondary battery.

[0067] In conducting the examinations, slurry composed of 85 wt. % of the lithium multiple oxide obtained as the active material, 8 wt. % of acetylene black, and 7 wt. % of PVDF (polyvinylidene fluoride) was prepared by use of NMP (N - methyl - pyrrolidone) as a solvent, and the slurry was applied to a aluminum foil, to be dried before press forming, thereby having obtained a cathode sample for use in evaluation of the lithium secondary battery.

[0068] The lithium secondary battery for use in the evaluation was the coin-battery model of 2032 type wherein the cathode sample was used for the cathode thereof while a lithium foil was used for an opposite electrode thereof, and for an electrolyte thereof, use was made of a solvent where a ratio of EC (ethylene carbonate) / DMC (dimethyl carbonate) was at 1 : 1, in which LiPF_6 at 1 mol was dissolved.

[0069] Using the lithium secondary battery for the evaluation, discharge capacity, and current load performance (discharge capacity obtained at discharge capacity obtained at 0.2C) were examined, and examination 0.5C / results, together with results for other lithium secondary batteries, are shown in Table 1.

(Working Example 4)

[0070] Lithium carbonate was dissolved into water to prepare an aqueous solution of lithium carbonate, into which carbon dioxide gas was blown, having thereby prepared 140 liter of an aqueous solution of lithium hydrogencarbonate with lithium carbonate concentration at 30 g / ℓ .

[0071] Subsequently, while stirring the aqueous solution of lithium hydrogencarbonate (at room temperature) at 300

rpm, 30 liter of an aqueous solution of a chloride of Ni, Mn, and Co, with composition of Ni : Mn : Co at 6 : 3 : 1 (the aqueous solution at room temperature, containing the chloride of Ni, Mn, and Co, at 1.5 mol/l in total concentration) was dripped into the aqueous solution of lithium hydrogencarbonate at an addition rate of 30 l/hr.

[0072] Next, through the intermediary of a vent pipe, air was passed at a flow rate of 10 l/min through the solution to which addition of the aqueous solution of the chloride was completed, and the carbon dioxide gas dissolved in the solution was driven out, having thereby raised a pH value from 6.7 to 8.3.

[0073] As a result of processing described, precipitate in fine particle form was precipitated in the solution, and upon examination of material in fine particle form, obtained by filtering and separating the precipitate to be subsequently further washed and dried, it was confirmed that the material in fine particle form was a multiple carbonate 7 µm in average grain size, with composition of Ni : Mn : Co at 6 : 3 : 1.

[0074] Further, in the multiple carbonate, obtained as above, Na content was found at 30 ppm, and S content also was found at 30 ppm.

[0075] Subsequently, heat treatment in the air at 650°C was applied to the multiple carbonate, obtained as above, for 15 hrs, whereupon there was obtained a multiple oxide in fine particles (7 µm in average grain size) with composition of Ni : Mn : Co at 6 : 3 : 1.

[0076] By mixing 100 g of the multiple oxide with 47.3 g of lithium carbonate, a mixture was obtained, and the mixture was fired in the air at 900°C for 10 hrs.

[0077] Measurements on powders of a compound obtained as above were made by the powder x-ray diffraction method, whereupon it was confirmed that the powders represented a layered lithium multiple oxide expressed by chemical formula $\text{Li Ni}_{0.6}\text{Mn}_{0.3}\text{Co}_{0.1}\text{O}_2$.

[0078] Further, the lithium multiple oxide powders were found at 7 µm in average grain size, and 0.6 m²/g in specific surface area, and Na content in the powders was at 30 ppm while S content in the powders was 40 ppm.

[0079] Then, examinations were conducted on the characteristics of a lithium secondary battery in which the lithium multiple oxide obtained as above was adopted as a cathode active material for the lithium secondary battery.

[0080] In conducting the examinations, slurry composed of 85 wt. % of the lithium multiple oxide obtained as the active material, 8 wt. % of acetylene black, and 7 wt. % of PVDF (polyvinylidene fluoride) was prepared by use of NMP (N-methyl-pyrrolidone) as a solvent, and the slurry was applied to a aluminum foil to be subsequently dried before press forming, thereby having obtained a cathode sample for use in evaluation of the lithium secondary battery.

[0081] The lithium secondary battery for use in the evaluation was the coin-battery model of 2032 type wherein the cathode sample was used for the cathode thereof while a lithium foil was used for an opposite electrode thereof, and for an electrolyte thereof, use was made of a solvent where a ratio of EC (ethylene carbonate)/DMC (dimethyl carbonate) was at 1 : 1, in which LiPF_6 at 1 mol was dissolved.

[0082] Using the lithium secondary battery for the evaluation, discharge capacity, and current load performance (discharge capacity obtained at 0.5C / discharge capacity obtained at 0.2C) were examined, and examination results, together with results for other lithium secondary batteries, are shown in Table 1.

(Working Example 5)

[0083] Lithium carbonate was dissolved into water to prepare an aqueous solution of lithium carbonate, into which carbon dioxide gas was blown, having thereby prepared 140 liter of an aqueous solution of lithium hydrogencarbonate with lithium carbonate concentration at 30 g/l.

[0084] Subsequently, while stirring the aqueous solution of lithium hydrogencarbonate (at room temperature) at 300 rpm, 30 liter of an aqueous solution of a chloride of Ni, Mn, and Co, with composition of Ni : Mn : Co at 5 : 3 : 2 (the aqueous solution at room temperature, containing the chloride of Ni, Mn, and Co, at 1.5 mol/l in total concentration) was dripped into the aqueous solution of lithium hydrogencarbonate at an addition rate of 30 l/hr.

[0085] Next, through the intermediary of a vent pipe, air was passed at a flow rate of 10 l/min through the solution to which addition of the aqueous solution of the chloride was completed, and the carbon dioxide gas dissolved in the solution was driven out, having thereby raised a pH value from 6.7 to 8.3.

[0086] As a result of processing described, precipitate in fine particle form was precipitated in the solution, and upon examination of material in fine particle form, obtained by filtering and separating the precipitate to be subsequently further washed and dried, it was confirmed that the material in fine particle form was a multiple carbonate 7 µm in average grain size, with composition of Ni : Mn : Co at 5 : 3 : 2.

[0087] Further, in the multiple carbonate, obtained as above, Na content was found at 40 ppm, and S content also was found at 20 ppm.

[0088] Subsequently, heat treatment in the air at 650°C was applied to the multiple carbonate, obtained as above, for 15 hrs, whereupon there was obtained a multiple oxide in fine particles (6 µm in average grain size) with composition of Ni : Mn : Co at 5 : 3 : 2.

[0089] By mixing 100 g of the multiple oxide with 45.9 g of lithium carbonate, a mixture was obtained, and the mixture

was fired in the air at 900°C for 10 hrs.

[0090] Measurements on powders of a compound obtained as above were made by the powder x-ray diffraction method, whereupon it was confirmed that the powders represented a layered lithium multiple oxide expressed by chemical formula $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$.

[0091] Further, the lithium multiple oxide powders were found at 6 μm in average grain size, and 0.5 m^2/g in specific surface area, and Na content in the powders was at 50 ppm while S content in the powders was 20 ppm.

[0092] Then, examinations were conducted on the characteristics of a lithium secondary battery in which the lithium multiple oxide obtained as above was adopted as a cathode active material for the lithium secondary battery.

[0093] In conducting the examinations, slurry composed of 85 wt. % of the lithium multiple oxide obtained as the active material, 8 wt. % of acetylene black, and 7 wt. % of PVDF (polyvinylidene fluoride) was prepared by use of NMP (N - methyl - pyrrolidone) as a solvent, and the slurry was applied to a aluminum foil to be subsequently dried before press forming, thereby having obtained a cathode sample for use in evaluation of the lithium secondary battery.

[0094] The lithium secondary battery for use in the evaluation was the coin-battery model of 2032 type wherein the cathode sample was used for the cathode thereof while a lithium foil was used for an opposite electrode thereof, and for an electrolyte thereof, use was made of a solvent where a ratio of EC (ethylene carbonate) / DMC (dimethyl carbonate) was at 1 : 1, in which LiPF_6 at 1 mol was dissolved.

[0095] Using the lithium secondary battery for the evaluation, discharge capacity, and current load performance (discharge capacity obtained at 0.5C / discharge capacity obtained at 0.2C) were examined, and examination results, together with results for other lithium secondary batteries, are shown in Table 1.

(Comparative Example 1)

[0096] Mixed powders prepared by mixing 37.3 g of NiO , 39.5 g of Mn_2O_3 , 40.1 g of Co_3O_4 , and 18.5 g of Li_2CO_3 , and the mixed powders were fired at 1,000°C for 1.0 hrs.

[0097] Subsequently, the mixed powders as fired were pulverized, having thereby obtained a layered lithium multiple oxide in fine particle form of 7 μm in average grain. In the lithium multiple oxide powders, Na content was found at 300 ppm, and S content was found at 3000 ppm.

[0098] Subsequently, examinations were conducted on the characteristics of a lithium secondary battery in which the lithium multiple oxide obtained as above was adopted as a cathode active material for the lithium secondary battery.

[0099] In conducting the examinations, slurry composed of 85 wt. % of the lithium multiple oxide obtained as the active material, 8 wt. % of acetylene black, and 7 wt. % of PVDF (polyvinylidene fluoride) was prepared by use of NMP (N - methyl - pyrrolidone) as a solvent, and the slurry was applied to a aluminum foil to be subsequently dried before press forming, thereby having obtained a cathode sample for use in evaluation of the lithium secondary battery.

[0100] The lithium secondary battery for use in the evaluation was the coin-battery model of 2032 type wherein the cathode sample was used for the cathode thereof while a lithium foil was used for an opposite electrode thereof, and for an electrolyte thereof, use was made of a solvent where a ratio of EC (ethylene carbonate) / DMC (dimethyl carbonate) was at 1 : 1, in which LiPF_6 at 1 mol was dissolved.

[0101] Using the lithium secondary battery for the evaluation, discharge capacity, and current load performance (discharge capacity obtained at 0.5C / discharge capacity obtained at 0.2C) were examined, and examination results, together with results for other lithium secondary batteries, are shown in Table 1.

(Working Example 6)

[0102] Lithium carbonate was dissolved into water to prepare an aqueous solution of lithium hydrogencarbonate, into which carbon dioxide gas was blown, having thereby prepared 140 liter of an aqueous solution of lithium hydrogencarbonate with lithium carbonate concentration at 30 g/l.

[0103] Subsequently, while stirring 30 liter of an aqueous solution of a chloride of Ni, Mn, and Co, with composition of Ni : Mn : Co at 1 : 1 : 1 (the aqueous solution at room temperature, containing the chloride of Ni, Mn, and Co at 1.5 mol/l in total concentration) at 300 rpm, the aqueous solution of lithium hydrogencarbonate (at room temperature), was charged into the aqueous solution of the chloride of Ni, Mn, and Co at a rate of 70 l/hr.

[0104] Next, through the intermediary of a vent pipe, air was passed at a flow rate of 10 l/min through the solution to which addition of the aqueous solution of lithium hydrogencarbonate was completed, and the carbon dioxide gas dissolved in the solution was driven out, having thereby raised a pH value from 6.9 to 8.0.

[0105] As a result of processing described, precipitate in fine particle form was precipitated in the solution, and upon examination of material in fine particle form, obtained by filtering and separating the precipitate to be subsequently further washed and dried, it was confirmed that the material in fine particle form was a multiple carbonate 10 μm in average grain size, with composition of Ni : Mn : Co at 1 : 1 : 1.

[0106] Further, in the multiple carbonate, obtained as above, Na content was found in a range of 20 to 50 ppm, and

S content was found at not more than 20 ppm. Subsequently, heat treatment at 650°C was applied to the multiple carbonate obtained as above for 15 hrs, whereupon there was obtained a multiple oxide 10 μm in average grain size) with composition of Ni : Mn : Co at 1 : 1 : 1.

[0107] By mixing 100 g of the multiple oxide with 45.3 g of lithium carbonate, a mixture was obtained, and the mixture was fired in the air at 1050°C for 5 hrs.

[0108] Measurements on powders of a compound obtained as above were made by the powder x-ray diffraction method, whereupon it was confirmed that the powders represented a layered lithium multiple oxide expressed by chemical formula $\text{Li Ni}_{1/3} \text{Mn}_{1/3} \text{Co}_{1/3} \text{O}_2$.

[0109] Further, the lithium multiple oxide powders were found at 10 μm in average grain size, and at 0.35 m^2/g in specific surface area, and Na content in the powders was in a range of 20 to 50 ppm while S content in the powders was not more than 20 ppm.

[0110] Then, examinations were conducted on the characteristics of a lithium secondary battery in which the lithium multiple oxide obtained as above was adopted as a cathode active material for the lithium secondary battery.

[0111] In conducting the examinations, slurry composed of 85 wt. % of the lithium multiple oxide obtained as the active material, 8 wt. % of acetylene black, and 7 wt. % of PVDF (polyvinylidene fluoride) was prepared by use of NMP (N - methyl - pyrrolidone) as a solvent, and the slurry was applied to a aluminum foil, to be subsequently dried before press forming, thereby having obtained a cathode sample for use in evaluation of the lithium secondary battery.

[0112] The lithium secondary battery for use in the evaluation was the coin-battery model of 2032 type wherein the cathode sample was used for the cathode thereof while a lithium foil was used for an opposite electrode thereof, and for an electrolyte thereof, use was made of a solvent where a ratio of EC (ethylene carbonate) / DMC (dimethyl carbonate) was at 1 : 1, in which LiPF_6 at 1 mol was dissolved.

[0113] Using the lithium secondary battery for the evaluation, discharge capacity, and current load performance (discharge capacity obtained at 0.5C / discharge capacity obtained at 0.2C) were examined, and examination results, together with results for other lithium secondary batteries, are shown in Table 1.

(Working Example 7)

[0114] Lithium carbonate was dissolved into water to prepare an aqueous solution of lithium carbonate, into which carbon dioxide gas was blown, having thereby prepared 140 liter of an aqueous solution of lithium hydrogencarbonate with lithium carbonate concentration at 30 g / ℓ .

[0115] Subsequently, while stirring the aqueous solution of lithium hydrogencarbonate (at room temperature) at 300 rpm, 30 liter of an aqueous solution of a chloride of Ni, Mn, Co, and Al, with composition of Ni : Mn : Co : Al at 0.317 : 0.317 : 0.317 : 0.05 (the aqueous solution at room temperature, containing the chloride of Ni, Mn, Co, and Al, at 1.5 mol/ ℓ in total concentration) was charged into the aqueous solution of lithium hydrogencarbonate at a rate of 30 ℓ /hr.

[0116] Next, through the intermediary of a vent pipe, air was passed at a flow rate of 10 ℓ /min through the solution to which addition of the aqueous solution of the chloride was completed, and the carbon dioxide gas dissolved in the solution was driven out, having thereby raised a pH value from 6.6 to 8.2.

[0117] As a result of processing described, precipitate in fine particle form was precipitated in the solution, and upon examination of material in fine particle form, obtained by filtering and separating the precipitate to be subsequently further washed and dried, it was confirmed that the material in fine particle form was a multiple carbonate (part of Al being in the form of hydroxide) 7 μm in average grain size, with composition of Ni : Mn : Co : Al at 0.317 : 0.317 : 0.317 : 0.05.

[0118] Further, in the multiple carbonate, obtained as above, Na content was found in a range of 20 to 50 ppm, and S content was found at not more than 10 ppm. Subsequently, heat treatment at 650°C was applied to the multiple carbonate, obtained as above, for 15 hrs, whereupon there was obtained a multiple oxide 7 μm in average grain size, with composition of Ni : Mn : Co : Al at 0.317 : 0.317 : 0.317 : 0.05.

[0119] By mixing 100 g of the multiple oxide with 45.2 g of lithium carbonate, a mixture was obtained, and the mixture was fired in the air at 1050°C for 5 hrs.

[0120] Measurements on powders of a compound obtained as above were made by the powder x-ray diffraction method, whereupon it was confirmed that the powders represented a layered lithium multiple oxide expressed by chemical formula $\text{Li Ni}_{0.317} \text{Mn}_{0.317} \text{Co}_{0.317} \text{Al}_{0.05} \text{O}_2$.

[0121] Further, the lithium multiple oxide powders were found at 7 μm in average grain size, and 0.41 m^2/g in specific surface area, and Na content in the powders was in a range of 20 to 50 ppm while S content in the powders was not more than 10 ppm.

[0122] Then, examinations were conducted on the characteristics of a lithium secondary battery in which the lithium multiple oxide obtained as above was adopted as a cathode active material for the lithium secondary battery.

[0123] In conducting the examinations, slurry composed of 85 wt. % of the lithium multiple oxide obtained as the active material, 8 wt. % of acetylene black, and 7 wt. % of PVDF (polyvinylidene fluoride) was prepared by use of NMP

(N - methyl - pyrrolidone) as a solvent, and the slurry was applied to a aluminum foil to be subsequently dried before press forming, thereby having obtained a cathode sample for use in evaluation of the lithium secondary battery.

[0124] The lithium secondary battery for use in the evaluation was the coin-battery model of 2032 type wherein the cathode sample was used for the cathode thereof while a lithium foil was used for an opposite electrode thereof, and for an electrolyte thereof, use was made of a solvent where a ratio of EC (ethylene carbonate) / DMC (dimethyl carbonate) was at 1 : 1, in which LiPF_6 at 1 mol was dissolved.

[0125] Using the lithium secondary battery for the evaluation, discharge capacity, and current load performance (discharge capacity obtained at 0.5C / discharge capacity obtained at 0.2C) were examined, and examination results, together with results for other lithium secondary batteries, are shown in Table 1.

[0126] It is evident from the results shown in Table 1 that according to the invention, it is possible to stably produce a cathode material with which there can be provided a lithium secondary battery excellent in both discharge capacity, and current load performance.

[0127] With the working examples described hereinbefore, there have been shown only examples involving the chloride containing Ni, Mn, and Co together, and the lithium multiple oxides, however, it has already been confirmed that similar excellent results can be obtained in the case of including the chloride containing Ni, Mn, or Co, alone, and the lithium multiple oxides, and the case of including the chloride containing at least two elements selected from the group consisting of Ni, Mn, and Co, and the lithium multiple oxides.

[0128] Further, with any of the working examples described hereinbefore, the chloride was subjected to the oxidation treatment, however, it has also been confirmed that similar results can be obtained even if the chloride is mixed directly with the lithium source to be subsequently fired.

[0129] Still further, there has been exhibited only Working Example 7 wherein Al has been added as an example in which other metal is added, it has also been confirmed that similar results can be obtained even in the case where at least one element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr is added

INDUSTRIAL APPLICABILITY

[0130] The invention can provide a cathode material for a lithium secondary battery (a precursor material for production of a cathode active material, and the cathode active material), with which it is possible to implement a lithium secondary battery capable of exhibiting excellent battery performance, and a method of stably producing the same.

Claims

1. A precursor material for a cathode material for a lithium secondary battery, being a carbonate expressed by chemical formula ACO_3 (where A is at least an element selected from the group consisting of Ni, Mn and Co) with respective contents of Na, and S, as impurity elements, at not more than 100 ppm in mass percentage.
2. A precursor material for a cathode material for a lithium secondary battery, being a mixture of carbonate expressed by chemical formula ACO_a (where A is at least an element selected from the group consisting of Ni, Mn and Co), and either or both of carbonate expressed by chemical formula DCO_3 (where D is at Least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), and hydroxide expressed by chemical formula D(OH) , an atomic ratio of an element D to the total of the element A and the element D $\{\text{D} / (\text{A} + \text{D})\}$ being in a range of 0 to 0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage.
3. A cathode material for a lithium secondary battery, being an Li-A-D-O based multiple oxide for the lithium secondary battery (where A is at least an element selected from the group consisting of Ni, Mn and Co, and D is at least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), an atomic ratio of the element D to the total of the element A and the element D $\{\text{D} / (\text{A} + \text{D})\}$ being in a range of 0 to 0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage.
4. A method of producing a precursor material for a cathode material for a lithium secondary battery, expressed by chemical formula ACO_3 (where A is at least an element selected from the group consisting of Ni, Mn and Co) with respective contents of Na, and S, as impurity elements, at not more than 100 ppm in mass percentage, said method comprising the steps of charging an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride into lithium carbonate suspension, and precipitating carbonate.

5. A method of producing a precursor material for a cathode material for a lithium secondary battery, being a mixture of carbonate expressed by chemical formula ACO_3 (where A is at least an element selected from the group consisting of Ni, Mn and Co), and either or both of carbonate expressed by chemical formula DCO_3 (where D is at least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), and hydroxide expressed by chemical formula $\text{D}(\text{OH})$, an atomic ratio of an element D to the total of the element A and the element D $\{\text{D} / (\text{A} + \text{D})\}$ being in a range of 0 to 0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage, said method comprising the steps of charging a mixed liquid composed of an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and an aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride into lithium carbonate suspension, and precipitating carbonate, or carbonate, and hydroxide.
6. A method of producing a precursor material for a cathode material for a lithium secondary battery composed of a carbonate expressed by chemical formula ACO_3 (where A is at least an element selected from the group consisting of Ni, Mn and Co) with respective contents of Na, and S, as impurity elements, at not more than 100 ppm in mass percentage, said method comprising the steps of preparing an aqueous solution of lithium hydrogencarbonate by blowing carbon dioxide gas into an aqueous solution of lithium carbonate, dripping an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride to the aqueous solution of lithium hydrogencarbonate, or dripping or charging the aqueous solution of lithium hydrogencarbonate into the aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and subsequently driving out dissolved carbon dioxide gas by aerating the aqueous solution, thereby raising a pH value of the aqueous solution to cause carbonate to be precipitated.
7. A method of producing a precursor material for a cathode material for a lithium secondary battery, being a mixture of carbonate expressed by chemical formula ACO_3 (where A is at least an element selected from the group consisting of Ni, Mn and Co), and either or both of carbonate expressed by chemical formula DCO_3 (where D is at least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), and hydroxide expressed by chemical formula $\text{D}(\text{OH})$, an atomic ratio of an element D to the total of the element A and the element D $\{\text{D} / (\text{A} + \text{D})\}$ being in a range of 0 to 0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage, said method comprising the steps of preparing an aqueous solution of lithium hydrogencarbonate by blowing carbon dioxide gas into an aqueous solution of lithium carbonate, dripping a mixed liquid of an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and an aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride to the aqueous solution of lithium hydrogencarbonate, or dripping or charging the aqueous solution of lithium hydrogencarbonate into the mixed liquid of the aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and the aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride, and subsequently, driving out dissolved carbon dioxide gas by aerating the aqueous solution, thereby raising a pH value of the aqueous solution to cause carbonate to be precipitated.
8. A method of producing a cathode material for a lithium secondary battery, being an Li-A-D-O based multiple oxide for the lithium secondary battery (where A is at least an element selected from the group consisting of Ni, Mn and Co, and D is at least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), an atomic ratio of the element D to the total of the element A and the element D $\{\text{D} / (\text{A} + \text{D})\}$ being in a range of 0 to 0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage, said method comprising the steps of charging a mixed liquid of an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and an aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride into lithium carbonate suspension, thereby precipitating carbonate, or carbonate, and hydroxide, and subsequently, mixing precipitate as obtained with a lithium source before firing, or applying oxidation treatment to the precipitate as obtained to be turned into an oxide, the oxide being mixed with the lithium source before firing.
9. A method of producing a cathode material for a lithium secondary battery, being an Li-A-D-O based a multiple oxide for the lithium secondary battery (where A is at least an element selected from the group consisting of Ni, Mn and Co, and D is at least an element selected from the group consisting of Mg, Al, Ti, Cr, Fe, Cu, and Zr), an atomic ratio of the element D to the total of the element A and the element D $\{\text{D} / (\text{A} + \text{D})\}$ being in a range of 0 to

0.1, and further, respective contents of Na, and S, as impurity elements, being not more than 100 ppm in mass percentage, said method comprising the steps of preparing an aqueous solution of lithium hydrogencarbonate by blowing carbon dioxide gas into an aqueous solution of lithium carbonate, dripping a mixed liquid of an aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and an aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride to the aqueous solution of lithium hydrogencarbonate, or dripping or charging the aqueous solution of lithium hydrogencarbonate into the mixed liquid of the aqueous solution containing at least one chloride selected from the group consisting of Ni chloride, Mn chloride, and Co chloride, and the aqueous solution of at least one chloride selected from the group consisting of Mg chloride, Al chloride, Ti chloride, Cr chloride, Fe chloride, Cu chloride, and Zr chloride, subsequently, driving out dissolved carbon dioxide gas by aerating the aqueous solution, thereby raising a pH value of the aqueous solution to cause carbonate, or carbonate and hydroxide to be precipitated, and mixing precipitate as obtained with a lithium source before firing, or applying oxidation treatment to the precipitate as obtained to be turned into an oxide, the oxide being mixed with the lithium source before firing.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/16416

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl.⁷ H01M4/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl.⁷ H01M4/00-4/62Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1926-1996 Jitsuyo Shinan Toroku Koho 1996-2004
Kokai Jitsuyo Shinan Koho 1971-2004 Toroku Jitsuyo Shinan Koho 1994-2004

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2002-313338 A (Sumitomo Metal Mining Co., Ltd.), 25 October, 2002 (25.10.02), Par. No. [0033] (Family: none)	1, 3 2, 4-9
X A	JP 2002-321921 A (Sony Corp.), 08 November, 2002 (08.11.02), Par. Nos. [0021] to [0032] (Family: none)	1, 3 2, 4-9
Y A	JP 5-343066 A (Mitsui Mining & Smelting Co., Ltd.), 24 December, 1993 (24.12.93), Claims 1, 2; Par. No. [0028] (Family: none)	3 1, 2, 4-9

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:
 "A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
 "Z" document member of the same patent family

Date of the actual completion of the international search
26 March, 2004 (26.03.04)Date of mailing of the international search report
13 April, 2004 (13.04.04)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/16416

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 10-182159 A (Tosoh Corp.), 07 July, 1998 (07.07.98), Claims 1, 3; Par. Nos. [0005], [0028] (Family: none)	3 1, 2, 4-9
Y A	JP 11-154512 A (Asahi Chemical Industry Co., Ltd.), 08 June, 1999 (08.06.99), Claim 1; Par. No. [0025] (Family: none)	3 1, 2, 4-9
A	EP 1225650 A2 (Kabushiki Kaisha Toshiba), 24 July, 2002 (24.07.02), & JP 2002-304994 A & US 2002/0150820 A1	1-9

Form PCT/ISA/210 (continuation of second sheet) (July 1998)